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Co-ion fluxes of simple inorganic ions in electrodialysis metathesis and conventional electrodialysis

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Abstract

The main functionality of ion-exchange membranes is to selectively permeate either cations or anions. However, co-ions may permeate as well to some extent through these membranes. For the production of chemicals with electrodialysis metathesis and conventional electrodialysis, these co-ion fluxes are a major source of impurities in the produced chemicals. The present paper studies the co-ion fluxes and the influence of operating parameters. The results clearly indicate that co-ion fluxes are predominately determined by the difference in ion concentration across the membrane. A more than linear increase in co-ion flux with respect to the ion concentration was observed. The current density has no significant influence on the co-ion fluxes. Therefore, a high current density leads to a smaller transport number of co-ions and improves the product purity in electrodialysis metathesis. Moreover, the co-ion flux can be decreased by the use of bulky counter-ions. In a conventional electrodialysis configuration, cation impurities are mainly caused by a diffusional flux. This flux is approximately three times larger than the co-ion flux. In contrast, the anion impurities are predominantly initiated by a co-ion flux and in magnitude smaller than the cation impurities.

1. Introduction

Ion-exchange membranes are polymeric membranes with charged groups attached to the polymer matrix [1]. Depending on the charge of the fixed groups, two types of ion-exchange membranes are to be distinguished: cation-exchange membranes, with negatively charged groups, and anion-exchange membranes, with positively charged groups. In cation-exchange membranes, the fixed negatively charged groups and the negatively charged anions in the membrane phase are in electrical equilibrium with the positively charged cations. The mobile cations are referred to as counter-ions; ions with the same charge as the fixed groups are denoted as co-ions. These co-ions are largely excluded from the polymer matrix due to the electrical repulsion with the fixed groups. Therefore, cation-exchange membranes preferentially permeate cations and retain anions. This phenomenon is known as Donnan exclusion [1-6].

In ideal permselective ion-exchange membranes co-ions should be completely excluded from the polymer matrix. However, in real membranes small amounts of co-ions are absorbed in the membrane phase. According to the Donnan exclusion theory the concentration of monovalent co-ions in ion-exchange membranes is inversely proportional to the concentration of fixed charged groups in the membrane [7] and proportional with the square of the ion concentration in the external solution [5]. The theory therefore predicts that a reduction in the concentration of the fixed charged groups should lead to a reduction in co-ion exclusion [8]. However, real ion-exchange membranes do not strictly obey the quadratic proportionality of the co-ion concentration with the external salt concentration. The Donnan exclusion theory assumes that the charge distribution in the membrane is homogeneous. Due to structural irregularities in actual membranes, small variations in the distribution of the charged groups result in a lower than calculated co-ion exclusion [8-12]. The local spatial variations increase with the volume fraction of water in the membrane. Membranes with a low water sorption therefore comply with the Donnan exclusion theory to a greater extent [8]. The co-ion concentration was found proportional to the external salt concentration with a power ranging from 1.2 to 1.5 [8, 9], constituting an intermediate value between an ideal membrane (with a power of 2) and an uncharged membrane (with a power of 1).

The quantity of counter and co-ions in ion-exchange membranes has been widely studied in the literature [8, 13-17]. For example, sorption of KCl and LiCl in three commercial available cation-exchange membranes was investigated by Nouri et al. over a concentration range from 0.1 to 3.0 M [15]. Diffusion coefficients of both counter and co-ions in cation-exchange membranes were determined. The authors found that the co-ion diffusion coefficient varied with the free water content of the membrane and is influenced by the internal interactions with the membrane. Geise et al. studied sorption of NaCl in sulfonated polymers and used the sorption data to develop a model predicting the overall salt uptake by the polymer [8]. Chakravarti studied the mobility and self-diffusion coefficient of the sulphate co-ion in a grafted cation-exchange membrane [16].

The permselectivity of an ion-exchange membrane is determined by the ratio of the transport of electrical charges by the counter-ions and the total electrical charges through the membrane [10]. A fast and simple method to determine the permselectivity is the determination of the membrane potential. In this case, the electrical potential difference is measured between two salt solutions with different concentrations and separated by a membrane. These measurements are conducted in absence of an electrical field; therefore, no concentration polarisation at the membrane-water interface occurs. Moreover, because water transport across the membrane is not taken into account, the measured permselectivity is referred to as the "apparent" permselectivity [18-20]. Furthermore, the co-ion flux varies with varying concentration. Therefore, this method yields a transport number which is an average of both salt concentrations [21]. The method is frequently used in the literature to

determine transport and transference numbers of both counter and co-ions [22-28]. The transport number of an ion is the fraction of the current that is carried by the ion; the transference number indicates the number of moles transported per mole of electrons [10].

A second method to determine the transport number of counter and co-ion is the use of the Hittorf cell [17, 29, 30]. In a Hittorf cell a membrane is placed between two electrodes. The ion flux through the membrane is measured by the increase or decrease in ion concentration. The permselectivity obtained with this method is referred to as the “true” transport number [10]. Bruce et al. used a Hittorf cell to determine actual transference numbers in amorphous poly(ethylene oxide)-based polymer electrolyte containing lithium perchlorate at 120°C [29]. The transport numbers of mobile ions in phenol-sulfonic cation-exchange membranes have been studied by Meares et al. [31]. The authors found that the transport number of chloride co-ions was much larger if bivalent counter-ions are used instead of monovalent counter-ions.

The use of electrodialysis for the production of chemicals, e.g., by electrodialysis metathesis [32], is restricted by the poor product purity. This is caused by the limited permselectivity of ion-exchange membranes. A profound understanding of the co-ion fluxes in electrodialysis metathesis and conventional electrodialysis is necessary for the exploitation of this technology. Experiments are performed in a metathesis stack and a conventional electrodialysis stack to achieve similar experimental conditions (e.g., concentration polarization, linear flow velocity, etc.) as in a stack used for the production of chemicals. To the best of the authors' knowledge, a comparison between the magnitude of the unwanted fluxes and the influence of the stack configurations was not made earlier. Therefore, this paper offers new insights in the origin of impurities in the electrodialysis process. The first aim of this paper is to investigate the co-ion fluxes in detail and to find an optimal working range for the production of chemicals. Therefore, the influence of different operating parameters such as the salt concentration and the current density on the co-ion fluxes in an electrodialysis metathesis configuration is studied. As a consequence of electroneutrality, ion fluxes in a stack depend on all fluxes occurring in a stack. In the second part of this study, the two setups in which the production of chemicals is possible are compared. The co-ion flux in a conventional electrodialysis setup is compared with the fluxes found in a metathesis setup.

2. Materials and methods

2.1. Electrodialysis equipment

All experiments were carried out with a PCCell ED 64-002 stack manufactured by PCCell GmbH, Heusweiler, Germany. Each membrane has an active surface area of 0.0064 m²; all membranes are separated by spacers with a thickness of 0.5 mm. Membranes and spacers were supplied by PCA (PolymerChemie Altmeier GmbH, Heusweiler, Germany). An overview of the characteristics of the membranes, which was provided by the manufacturer, is given in

Table 1. The transport of co-ions is investigated in the PC-SA and the PC-SK membranes. The PC-SC membrane is only used to separate the stack configuration from the electrode rinsing solution. Between the experiments membranes are stored in a 0.25 M NaCl solution.

Table 1: Overview of the characteristics of PCA membranes, namely standard anion-exchange membranes (PC-SA), standard cation-exchange (PC-SK) and reinforced cation-exchange membranes (PC-SC).

| Membrane | PC-SA | PC-SK | PC-SC |
|--|--------|--------|--------|
| Thickness [μm] | 90-130 | 90-130 | 90-130 |
| Ion-exchange capacity [mequiv.g^{-1}] | | | |
| weak | ca 0.4 | | |
| strong | ca 1.1 | ca 1.2 | ca 1.1 |
| Chemical stability (pH) | 0-9 | 0-9 | 0-12 |
| Permselectivity ^a | > 0.93 | > 0.95 | > 0.92 |

^aDetermined as the membrane potential between a 0.1 and 0.5 M KCl solution.

The experimental setup was described in detail elsewhere [33]. In brief, the setup consists of three vessels for two salt streams and the electrode rinsing solution. All experiments are carried out in batch mode. The flow rate of the two salt streams was 6 L h^{-1} per compartment, the flow rate of the electrode rinsing solution was 150 L h^{-1} . The flow rates correspond with a linear flow velocity of $4.2 \cdot 10^{-2} \text{ m s}^{-1}$ for the two salt stream and $5.2 \cdot 10^{-1} \text{ m s}^{-1}$ for the electrode rinsing solution. The effects of osmosis and electro-osmosis were taken into account by measuring the change in volume height in the cylindrical vessels. During each experiment a constant current density is applied to achieve desalination. The current was set by using a DC adjustable power source (Delta Elektronika ES030-10, Zierikzee, The Netherlands).

2.2. Electrodialysis metathesis experiments

2.2.1. Stack configuration

Figure 1 shows the cell configuration used to determine the flux of co-ions through ion-exchange membranes. This figure specifies the configuration to test the permselectivity of anion-exchange membranes for cations. The permselectivity of cation-exchange membranes is tested in an analogous configuration where the anion-exchange membranes are replaced by cation-exchange membranes. For the investigation of anion-exchange membranes, four membranes are placed between the two electrodes. Two different salt streams, e.g., an initial pure sodium chloride and potassium chloride solutions, are circulated through these compartments in an alternating pattern. Due to the applied voltage difference and the anion membranes, chloride ions are the only counter-ions that are transported through the membranes, indicated as full arrows. Because of the concentration gradient in co-ions a small amount of cations is transported through these anion membranes, indicated as dotted arrows. As a result of the use of a different cation in both salt streams, the change of for example the

sodium concentration in the potassium chloride solution can be determined accurately. The increase of sodium concentration in the initial potassium chloride solution is used to calculate the flux of sodium through the anion-exchange membranes.

At each side of the four anion-exchange membranes a cation-exchange membrane is placed to separate the cell configuration from the electrode rinsing solution. In each experiment a 1 mol.L^{-1} sodium sulphamate or 1 mol.L^{-1} potassium sulphamate solution is used. The choice of the cation (either sodium or potassium) in the electrode rinsing solution depends on the cations used in the metathesis configuration. If a potassium flux is determined a sodium sulphamate solution is used and vice versa. In case of sodium sulphamate as the electrode rinsing solution each side of the electrode rinsing solutions is neighbouring an initial pure sodium chloride solution, as can be seen in Figure 1. Therefore, no interference of the sodium or potassium concentration caused by the sodium salt in the electrode rinsing solution is to be expected.

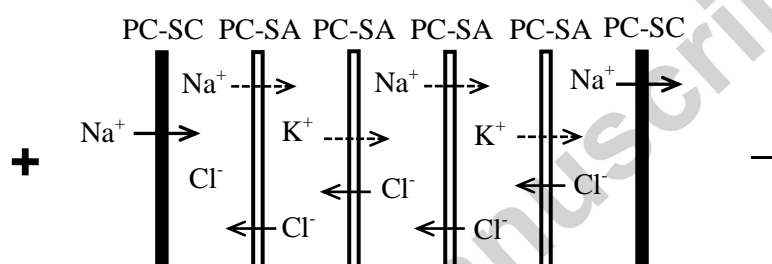


Figure 1: Cell configuration to determine the permselectivity of anion-exchange membranes (PC-SC: reinforced cation membrane, PC-SA: standard anion-exchange membrane, full arrows: transport of counter-ions, dotted arrows: transport of co-ions).

2.2.2. Experimental setup

A set of six experiments was used to investigate the permselectivity of the membranes for different anions or cations. An overview of the experimental setup for anion-exchange membranes is given in Table 2. The set consists of a 2^2 design of experiments with one centerpoint. The centerpoint is replicated one time to test the repeatability of the results. The anion concentration, in this case the chloride concentration, is varied from 0.5 to 2 mol.L^{-1} . For example, if sodium chloride is used, the concentration is varied from 0.5 to 2 mol.L^{-1} NaCl. If calcium chloride is used, the concentration varies from 0.25 to 1 mol.L^{-1} CaCl_2 . The current density is varied from 150 to 500 A.m^{-2} . In every experiment, the initial volume of both salt streams is 1 L. Each experiment was performed during 2 hours. Samples of both vessels were taken at the beginning and at each interval of 40 minutes.

Table 2: Experimental setup to test the permselectivity of anion-exchange membranes in electrodialysis metathesis.

| Anion concentration [mol.L ⁻¹] | Current density [A.m ⁻²] |
|--|--------------------------------------|
| 0.5 | 150 |
| 0.5 | 500 |
| 2 | 150 |
| 2 | 500 |
| 1.25 | 325 |

The experimental setup was used for different combinations of salt streams; an overview is given in Table 3. In the first three series the co-ion flux of sodium, potassium and calcium in PC-SA membranes were studied. In the fourth series the influence of the type of counter-ion on the co-ion flux was investigated. The co-ion fluxes of sodium and potassium were compared with the chloride counter-ion in the first series and an acetate counter-ion in the fourth series. In the fifth series the co-ion fluxes of chloride and nitrate in the PC-SK membrane was investigated in the presence of a sodium counter-ion. In the sixth series the sodium counter-ion is replaced with a potassium counter-ion to determine the influence of these counter-ions. The effect of the investigated operating parameters on the co-ion fluxes and the comparison between the different series is performed by a regression analysis. Only the effects with a t-value larger than the tabulated t-value with a significance level of 95% are considered as significant.

Table 3: Overview of the experiments in the metathesis configuration.

| Series | Compartment 1 | Compartment 2 | Membrane |
|--------|---------------|-------------------|----------|
| 1 | NaCl | KCl | PC-SA |
| 2 | NaCl | CaCl ₂ | PC-SA |
| 3 | KCl | CaCl ₂ | PC-SA |
| 4 | NaAc | KAc | PC-SA |
| 5 | NaCl | NaNO ₃ | PC-SK |
| 6 | KCl | KNO ₃ | PC-SK |

2.3. Conventional electrodialysis experiments

To compare the magnitude of the co-ion fluxes in electrodialysis metathesis with the magnitude of co-ion fluxes in a conventional electrodialysis setup a series of experiments were performed. In these experiments cation and anion-exchange membranes were placed in an alternating pattern, forming a diluate and concentrate stream. These experiments were performed for potassium and nitrate; an overview of the experimental conditions is given in

Table 4. The co-ion fluxes in this setup are caused by the transport of ions from the concentrate to the diluate stream. The co-ion flux is measured from the increase in the potassium and nitrate concentration in the diluate stream.

Table 4: Experimental conditions in the conventional electrodialysis experiments.

| Diluate composition | Concentrate composition | Current density [A.m^{-2}] |
|------------------------------------|---|---------------------------------------|
| 1 L 2.3 mol.L^{-1} NaCl | 2 L 2 mol.L^{-1} KNO_3 | 500 |
| 1 L 0.59 mol.L^{-1} NaCl | 2 L 0.5 mol.L^{-1} KNO_3 | 150 |

To achieve similarity with the experimental setup in the metathesis experiments (cf. Figure 1); diluate concentrations were chosen to achieve an average concentration of approximately 2 and 0.5 mol.L^{-1} during the experiment. The diluate volume is limited to only 1 L to ensure the accuracy of the measured concentration of potassium and nitrate. The concentrate volume was chosen sufficiently large (2 L) to ensure the KNO_3 concentration is changed as little as possible. Two repeating units with each one concentrate and diluate compartment were used in one stack. The experiments were performed during 60 minutes. Samples were taken at the beginning and at each interval of 15 minutes. In these experiments, a 1 mol.L^{-1} sodium sulphamate solution was used as the electrode rinsing solution.

Preliminary experiments showed a non-linear increase of the potassium and nitrate concentration in the diluate as a function of time. Potassium and nitrate are transported from the concentrate to the diluate as co-ions through anion-exchange and cation-exchange membranes, respectively. In the diluate these ions are transported as counter-ions according to the applied electrical field. Subsequently, the increase in potassium and nitrate concentration in the diluate compartment is higher in the beginning of the experiment. Therefore, co-ion fluxes were calculated from the increase in potassium and nitrate concentration in the first interval from 0 to 30 minutes.

In addition to these experiments similar experiments were performed in a four compartment electrodialysis setup to investigate and quantify a possible diffusion flux from the concentrate stream towards the diluate. The setup of this four compartment setup is shown in Figure 2. Two repeating units were used in one stack. In analogy to the conventional setup, the co-ion flux is caused by the transport of ions through a membrane with the same charge and in the same direction as the applied electrical field. In this setup the co-ion flux of potassium was measured as the increase in potassium concentration in the diluate 2 compartment, the co-ion flux of chloride was measured as the increase in nitrate concentration in the diluate 1 compartment. In a conventional electrodialysis setup, ions in the concentrate are possibly also transferred to the diluate compartment by a diffusion flux, which has the opposite direction to the applied electrical field. The diffusion flux of potassium was measured as the

increase of potassium concentration in the diluate 1 compartment, the diffusion flux of nitrate was measured as the increase of nitrate concentration in the diluate 2 compartment.

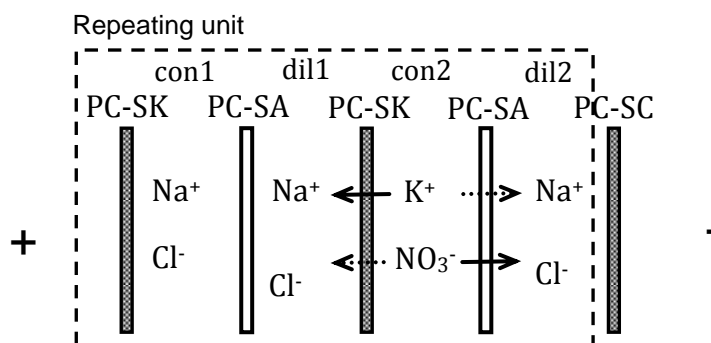


Figure 2: Cell configuration to determine the co-ion and diffusion flux in a conventional electrodialysis setup (full arrows: diffusion flux, dotted arrows: co-ion flux).

2.4. Analytical methods

The sodium and potassium concentration was measured by means of atomic emission spectroscopy; the calcium concentration was determined by means of atomic absorption spectroscopy. For the determination of all cations a Unicam AAS Solar 989 (ThermoFisher Scientific, USA) was used. The chloride concentration was measured by an argentometric titration with potentiometric end point detection. For this titration a METROHM 716 DMS Titrino (Metrohm, Switzerland) was used. The nitrate concentration was determined spectrophotometrically at a wavelength of 220 nm [34], for which a Varian Cary 100 BIO (Varian, USA) was used.

2.5. Data analysis

The flux of co-ions \dot{n}_{co-ion} [mol.s⁻¹.m⁻²] was calculated using eq. 1.

$$\dot{n}_{co-ion} = \frac{c_{co-ion,2} V_2 - c_{co-ion,1} V_1}{(t_2 - t_1) A N} \quad (1)$$

With c the co-ion concentration in the initial co-ion free compartment [mol.L⁻¹], V the volume of the co-ion free compartment [L], t the time [s], N the number of membranes tested, i.e., 2 [-] and A the surface area of one membrane [0.0064 m²]. The subscripts 1 and 2 refer to the point in time when the variable is studied. Error bars represent the standard deviation on the co-ion flux, measured during one experiment (four values). The transport number of co-ions T_{co-ion} was calculated by the ratio of the co-ion flux and the total ion flux carried by the applied current density (cf. eq. 2) [10].

$$T_{co-ion} = \frac{\dot{n}_{co-ion}}{\frac{i A N}{n F}} \quad (2)$$

With i the current density [A.m⁻²], n the valence of the co-ion [-], F the Faraday constant [96485 C.mol⁻¹]. The sum of the transport number of counter and co-ions must be 1. Eq. 3 calculates the transport number of counter-ions.

$$T_{\text{counter ion}} = 1 - T_{\text{co-ion}} \quad (3)$$

During the experiments the pH of all salt streams was monitored. Because no pH changes occurred, the limiting current density in none of the experiments was exceeded.

3. Results and discussion

3.1. Permselectivity of PC-SA membranes

3.1.1. Co-ion flux of sodium, potassium and calcium

The co-ion flux of sodium in PC-SA membranes was studied in two different series of experiments (series 1 and 2) and in the presence of the chloride counter-ion. In the first series the co-ion flux of sodium and potassium were simultaneously determined, in the second series the flux of sodium and calcium were determined (cf. Figure 3).

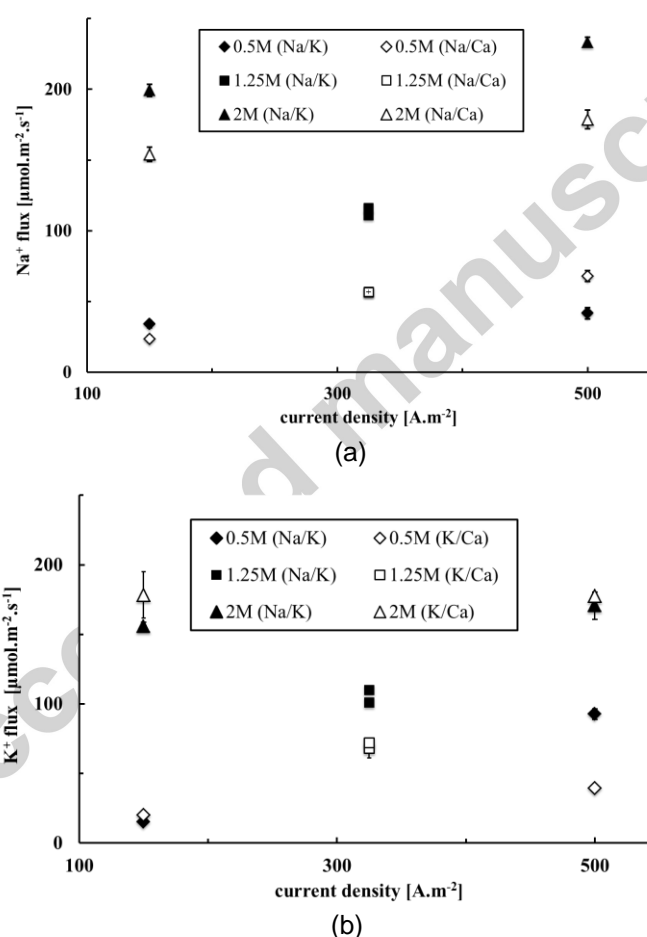


Figure 3: Co-ion flux of sodium (a) and potassium (b) in PC-SA membranes (counter-ion: chloride).

For both setups a pareto plot confirms that a variation in NaCl concentration has a significant influence on the co-ion flux. An increase in ion concentration in the external solution with a factor four leads to an increase of the co-ion flux with approximately a factor six. The large increase is caused by the density of charged groups in the membrane, which is an equal value in contact with different salt concentrations. The increase in ion concentration in the

external solution also results in an increase of the co-ion concentration in the solution. In case of high salt concentrations, the co-ions encounter relatively less repulsion by the fixed cationic groups in the anion-exchange membrane. The more than linear increase in co-ion flux is also predicted by the Donnan exclusion theory. In an ideal ion-exchange membrane the co-ion concentration of monovalent ions in the membrane matrix is proportional to the external salt concentration to a power of two. According to the measurements in Figure 3a in a Na^+/K^+ stack, the co-ion flux in PC-SA membranes has a power law slope of 1.25 ± 0.07 with respect to the ion concentration in solution. This is a value similar to the slope found for the dependence of the membrane's ion concentration to the solution's ion concentration in other commercial ion-exchange membranes [35].

For both salt concentrations an increase in current density results in only a small increase in co-ion flux. In case of high concentration gradients, co-ion transport across a membrane is predominantly driven by a difference in salt concentration rather than an electrical potential difference. A statistical analysis verified that the difference in sodium flux in both setups was not significant.

To explain the differences in co-ion flux of the different ions studied, an overview of the transport properties of these ions is given in Table 5. In this table, the Stokes radius represents the hydrated ion radius in solution [36]. The co-ion flux of potassium in PC-SA membranes shows an analogous behaviour as sodium (cf. Figure 3b). The flux is hardly influenced by the applied current density and strongly depends on the ion concentration in the solution. The co-ion fluxes of sodium and potassium are not significantly different in PC-SA membranes. These similar fluxes of both cations are remarkable. The hydrated ion radius of potassium is smaller and potassium has a higher molar ion conductivity than sodium. Both facts suggest that the PC-SA membrane should have a lower permselectivity for potassium and therefore a higher co-ion flux of potassium. However, a lack of counter-ion selectivity between potassium and sodium was reported earlier for cation-exchange membranes [37] and indicates that both cations have a similar transport rate in a membrane matrix.

Table 5: Transport properties of the ions studied at 298.15K [38].

| Ion | Na^+ | K^+ | Ca^{2+} | Cl^- | NO_3^- | Ac^- |
|---|---------------|--------------|------------------|---------------|-----------------|---------------|
| $r_{\text{Stokes}} [\text{nm}]$ | 0.184 | 0.125 | 0.155 | 0.121 | 0.129 | 0.225 |
| $\lambda_l^\infty [\text{cm}^{-1} \Omega^{-1} \text{mol}^{-1}]^a$ | 50.1 | 73.5 | 119.0 | 76.4 | 71.5 | 40.9 |

^aLimiting molar ion conductivity

The co-ion flux of calcium in PC-SA membranes is shown in Figure 3. The same tendency with respect to the current density is observed. The co-ion flux is hardly influenced by the applied current density. As can be seen in Figure 4, there is a large difference in flux in comparison with Figure 3. The calcium flux is much lower with respect to the flux of sodium

and potassium. Nevertheless, calcium ions have a divalent charge and are therefore stronger influenced by the electrical field. The divalent charge and the lower external calcium concentration (only half of the potassium and sodium concentration) also results in a stronger repulsion by the fixed charged cation groups and in a net decrease of the co-ion flux.

In contrast, another behaviour is observed for the dependency of the co-ion flux to the calcium concentration in the external solution. A very low calcium flux is noticed for the 0.25 M CaCl_2 solutions, while a strong increase is observed for an increase in calcium concentration. This tendency is also observed in the calcium concentration in anion-exchange membranes as predicted by the Donnan exclusion theory (cf. Appendix A). Because of the divalent charge of the calcium ion, the calcium concentration in the membrane is proportional to the third power of the external concentration. Therefore, a stronger increase in co-ion flux is observed in comparison with monovalent co-ions. Using the obtained results (Figure 4, $\text{Na}^+/\text{Ca}^{2+}$ stack), a power law slope of 2.36 ± 0.09 is found for the calcium flux in PC-SA membranes.

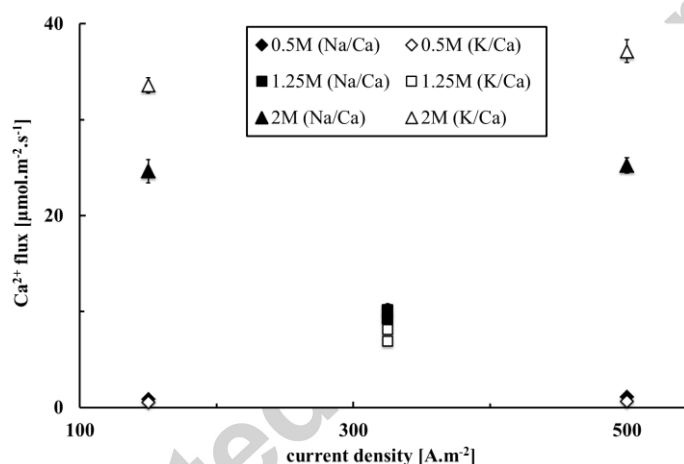


Figure 4: Co-ion flux of calcium in PC-SA membrane (counter-ion: chloride).

3.1.2. Transport number of co-ions

An overview of the transport number of sodium, potassium and calcium in PC-SA membranes is shown in Figure 5. The lowest transport numbers are found for the lowest ion concentration. With an increase in current density, the overall ion flux across the membrane is proportionally increased. A higher current density leads to a higher counter-ion flux and therefore a lower co-ion transport number. To achieve the highest transport number of counter-ions and an optimal performance of an ion-exchange membrane, it is therefore recommended to have low salt concentrations and to use high current densities.

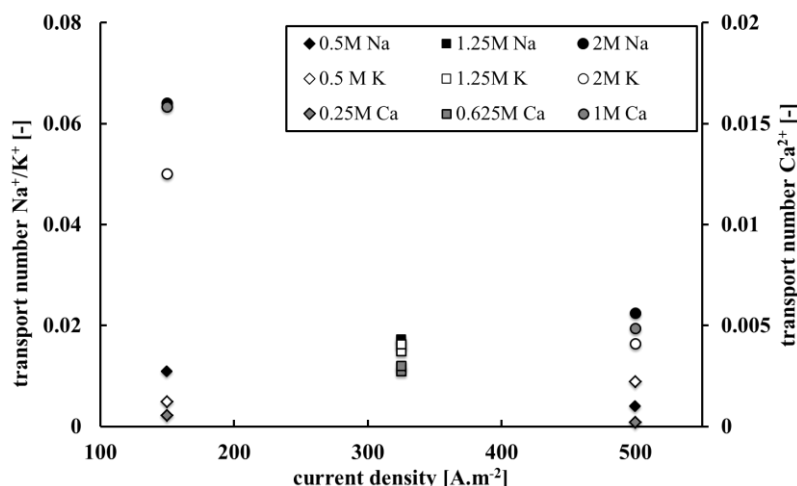


Figure 5: Transport number of the co-ion flux of sodium, potassium and calcium in PC-SA membrane.

According to the characteristics of the PC-SA membrane provided by the manufacturer, the apparent permselectivity or the transport number of the counter-ions should be above 0.93. Therefore, the transport number of co-ions should be below 0.07. In Figure 5, it can be seen that for all studied cations the transport number complied with the assumption for all studied concentrations and current density.

3.2. Co-ion flux of nitrate and chloride in PC-SK membranes

Similarly, the co-ion fluxes of anions, namely chloride and nitrate, were determined for standard cation-exchange membranes (PC-SK). An overview of the fluxes is given in Figure 6. A regression analysis demonstrates that the co-ion fluxes of chloride and nitrate are not significantly different for the PC-SK membrane. As can also be observed in Table 4, the chloride and nitrate ion have a similar hydrated ion radius and molar ion conductivity. In this case, the transport properties of ions in aqueous solutions correspond with the transport rate in the membrane matrix.

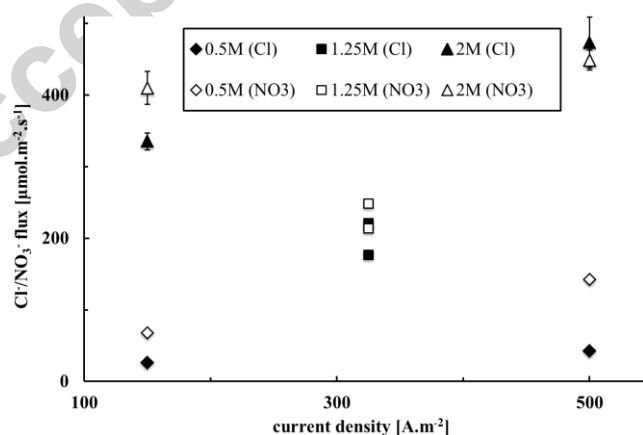


Figure 6: Co-ion flux of nitrate and chloride in the PC-SK membrane (Counter-ion: sodium).

Compared to the anion-exchange membranes a higher co-ion flux in cation-exchange membranes is observed. According to the data provided by the manufacturer, both membrane have a similar ion exchange capacity (Table 1). The transport properties of potassium are also similar to that of chloride and nitrate. The difference in co-ion flux can be caused due to a difference in swelling behaviour of both membranes, which leads to a difference in concentration of the fixed charged groups.

3.3. Influence of the type of counter-ion

In Figure 7, a comparison is made between the co-ion fluxes of chloride and nitrate through cation-exchange membranes in the presence of the sodium or potassium counter-ion. For all observed concentrations and current densities, the potassium counter-ion yields a higher co-ion flux of chloride and nitrate in comparison with the sodium counter-ion. The co-ion flux in an ion-exchange membrane is oriented in the opposite direction to the flux of counter-ions. As can be seen in Table 5, potassium has a smaller hydrated radius than sodium. Therefore, a counter-ion flow of potassium presumably results in less steric hindrance than a sodium counter-ion flow. Thus a higher co-ion flux is obtained with potassium. This figure also illustrates the difference between sodium and potassium as co-ion and counter-ion. As a counter-ion there is a large difference in co-ion flux, where as a co-ion no significant difference in co-ion flux is observed.

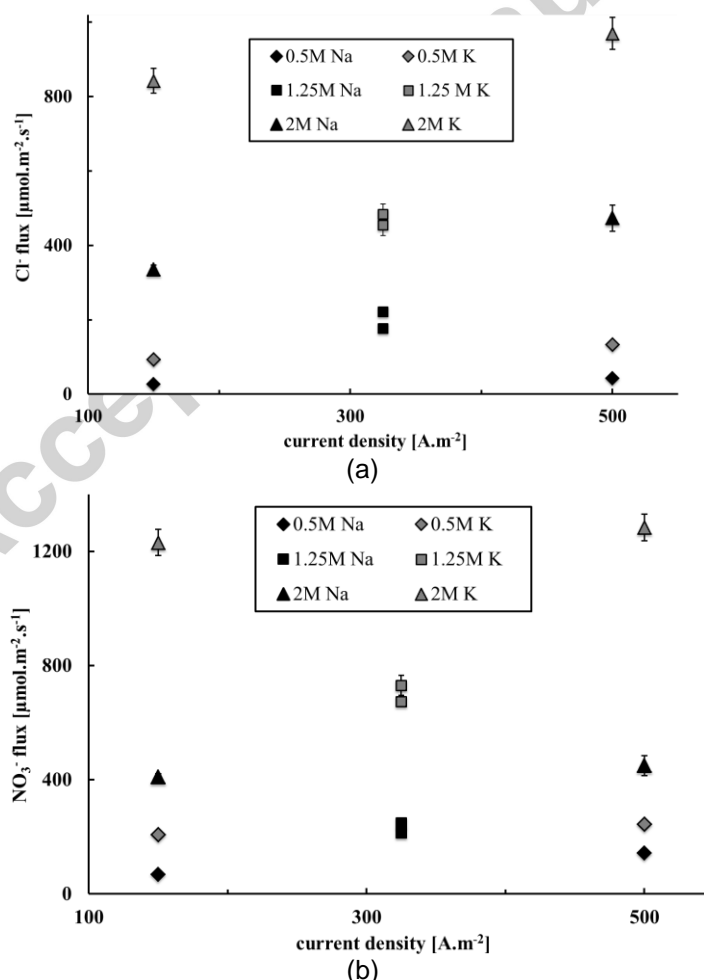
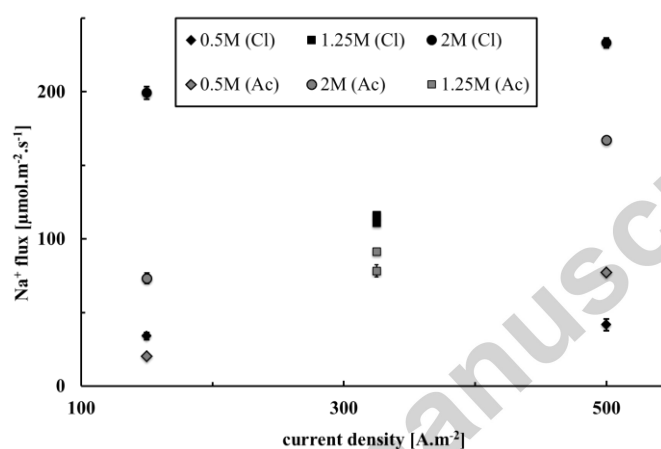
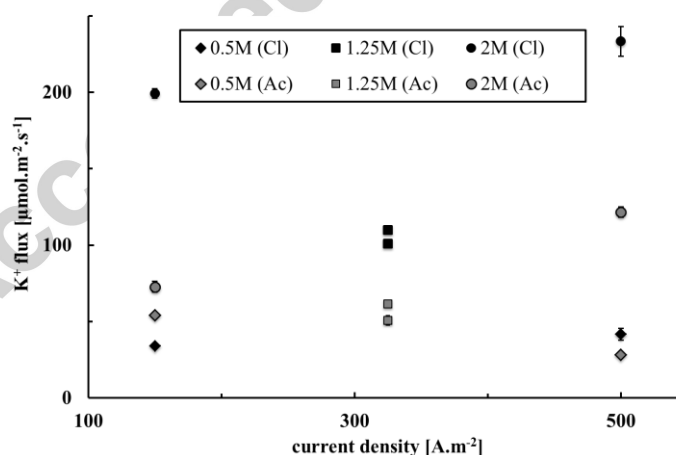


Figure 7: Co-ion flux of chloride (a) and nitrate (b) in PC-SK membranes in the presence of the sodium or potassium counter-ion.

In Figure 8, the co-ion flux of sodium and potassium is studied with a varying counter-ion. The chloride anion is here replaced with an acetate ion. As can be seen in Table 5, the acetate anion has a larger hydrated ion radius than chloride. In Figure 8, the difference in counter-ion results in a different co-ion flux of both potassium and sodium. Due to the larger steric hindrance of the acetate ion, a smaller co-ion flux is observed in comparison with the chloride counter-ion. For the acetate counter-ion, only a small difference in co-ion flux for different external salt concentrations is observed. Because of the large radius of the acetate anion, an increase in external salt concentration only results in a small increase in acetate concentration in the membrane. Due to electroneutrality in the membrane, the amount of additional co-ions, needed to compensate the increase in counter-ion, is small. Therefore, only a small increase in co-ion flux is observed for an increase in external salt concentration.



(a)



(b)

Figure 8: Co-ion flux of sodium (a) and potassium (b) in PC-SA membranes in the presence of chloride or acetate counter-ion.

3.4. Co-ion flux in conventional electrodialysis

In these experiments the co-ion fluxes of potassium and nitrate in a conventional electrodialysis setup were determined. A comparison of the co-ion fluxes in a metathesis and conventional configuration is shown in Figure 9. The nitrate co-ion fluxes in both setups have similar values and the same tendency in these results is observed. In contrast, the co-ion flux of potassium amounts to much higher values in the conventional electrodialysis setup in comparison with the metathesis configuration. The co-ion flux in both setups has approximately the same slope, an increased co-ion flux is presumably caused by a diffusion flux from the potassium in the concentrate through a cation-exchange membrane, in an opposite direction as the applied electrical field.

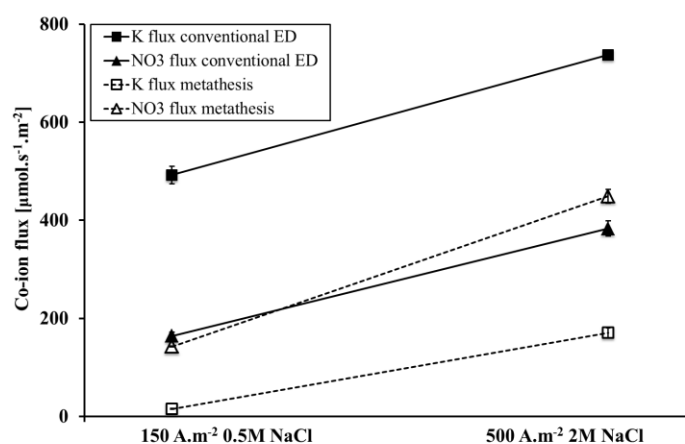


Figure 9: Comparison of the co-ion flux of potassium and nitrate in PC-SA and PC-SK membranes in a conventional and the metathesis setup.

A four compartment stack was used to quantify both the diffusion and the co-ion flux. In Figure 10 an overview of the flux of potassium measured in the metathesis, conventional and four compartment stack is given. The sum of the co-ion flux and diffusion flux in the four compartment stack approximates the flux measured in a conventional two compartment stack. It can also be seen that the co-ion fluxes in the four compartment and in the metathesis configuration approximately have the same value. In a practical situation, it is likely that high concentration gradients occur because the production of high concentrated salt streams is preferred. In this case, large diffusion flux of cations influences the purity of the obtained salt streams. If a chemical compound is produced by conventional electrodialysis, it would be more contaminated by cationic than anionic impurities.

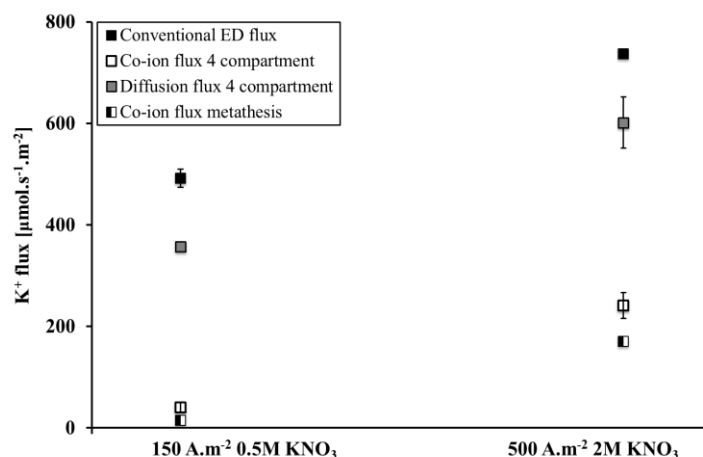


Figure 10: Overview of all fluxes of potassium in PC-SA and PC-SK membranes.

4. Conclusions

In the present paper, the co-ion fluxes of various inorganic anions and cations through respectively cation and anion-exchange membranes have been studied. Except for the acetate counter-ion, it was found that the co-ion fluxes for all ions tested are predominately determined by the external salt concentration. An increase in current density does not result in a significant increase in co-ion flux. For bivalent cations, a much smaller (more than five times) co-ion flux is observed in comparison with monovalent cations. Moreover, for divalent co-ions a stronger increase in flux is observed in comparison with monovalent ions for an equal increase in external salt concentration. This observation is in accordance with the co-ion concentration in the membrane, as predicted by the Donnan exclusion theory. The co-ion flux in cation-exchange membranes is larger than in anion-exchange membranes.

Secondly, the influence of the counter-ion on the co-ion flux was discussed. Due to the smaller hydrated radius of potassium compared to sodium, the co-ion flux of both nitrate and chloride are higher when potassium is used as the counter-ion instead of sodium. With the use of an acetate counter-ion instead of chloride a similar tendency is observed. The large ion radius results in a lower co-ion flux. Due to the large hydrated radius of acetate, only a small difference in co-ion flux of sodium and potassium is observed for an increase in external salt concentration.

Finally, the unwanted fluxes in a conventional electrodialysis setup were compared with the co-ion flux in a metathesis configuration. The cation flux is larger in a conventional setup than in a metathesis setup. The cation flux is composed of a diffusion flux which is at least three times larger than the co-ion flux under the investigated experimental conditions. In contrast to the cations, the unwanted fluxes of anions are not significantly different in both setups and smaller in magnitude than the cation fluxes. A produced chemical compound is therefore contaminated more by cationic than by anionic impurities.

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A. Appendix

Concentration of monovalent and divalent ions in anion-exchange membranes

The concentration of monovalent co-ions in ion-exchange membranes is calculated by Equation 3 [7].

$$c_{co}^m = \frac{(c^s)^2}{X} \quad (3)$$

Where the superscript s refers the solution and superscript m to the membrane. X refers to the fixed charge density. In this formula can be seen that a high density of fixed charge groups leads to a low co-ion concentration in the membrane. A low salt concentration in the external solution also favours the Donnan exclusion of co-ions.

The concentration of divalent ions, for example calcium in anion-exchange membranes is calculated using the Donnan exclusion theory. The Donnan potential is determined by the difference in potential between the membrane and the solution.

$$\varphi_{Don} = \varphi_m - \varphi_s = \frac{R T}{z_i F} \ln \frac{a_i^s}{a_i^m} \quad (4)$$

An anion-exchange membrane is placed in a CaCl_2 solution. For all ions in solution the Donnan potential is equal. In case of low CaCl_2 concentrations, activities are replaced by concentrations.

$$\varphi_{Don} = \frac{R T}{z_{Cl^-} F} \ln \frac{c_{Cl^-}^s}{c_{Cl^-}^m} = - \frac{R T}{z_{Ca^{2+}} F} \ln \frac{c_{Ca^{2+}}^s}{c_{Ca^{2+}}^m} \quad (5)$$

$$\frac{c_{Cl^-}^s}{c_{Cl^-}^m} = \left(\frac{c_{Ca^{2+}}^m}{c_{Ca^{2+}}^s} \right)^{0.5} \quad (6)$$

In the membrane matrix there is electroneutrality between the fixed cation groups, the sorbed calcium and chloride ions.

$$c_{Cl^-}^m = X + 2 c_{Ca^{2+}}^m \quad (7)$$

In solution the calcium concentration is half of the chloride concentration.

$$c_{Ca^{2+}}^s = 2 c_{Cl^-}^s \quad (8)$$

Equation 7 and 8 are introduced in equation 6.

$$c_{Ca^{2+}}^m = \frac{0.25 (c_{Ca^{2+}}^s)^3}{(X + 2 c_{Ca^{2+}}^m)^2} \quad (9)$$

When the concentration of calcium ions in the membrane matrix is negligible in respect to the concentration of fixed ionic groups, Equation 9 can be further simplified to Equation 10.

$$c_{Ca^{2+}}^m = \frac{0.25 (c_{Ca^{2+}}^s)^3}{X^2} \quad (10)$$

In comparison with monovalent ions, the concentration of divalent co-ions is quadratically dependant of the charged groups density. Divalent co-ions are therefore more repulsed by the fixed ionic groups in the membrane matrix. The calcium concentration in the membrane is proportional to a power of 3 to the external concentration where the ion concentration of monovalent ions is proportional to a power of 2. The concentration of divalent ions at low concentrations will therefore be smaller than an equal concentration of monovalent ions. However at higher external concentrations the calcium concentration in the membrane will increase faster than the concentration of a monovalent ion.

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Highlights

- Co-ion flux is predominately determined by the ion concentration
- Bulky counter-ions result in a lower co-ion flux
- Diffusion fluxes of cations are larger than co-ion fluxes in a conventional setup
- In produced chemicals cationic impurities are higher than anionic impurities

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